

CASE EL/2-22733/A/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
GERARDUS DE KEYZER ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 03/08654

Group Art Unit: 1712
Examiner: T. J. Kugel

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FOR: LIQUID CRYSTAL DISPLAY AND COLOUR

FILTER WITH IMPROVED

TRANSPARENCY FOR GREEN LIGHT

U.S. APPLICATION NO: 10/523,742

35 USC 371 DATE: FEBRUARY 2, 2005

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

I, Gerardus de Keyzer, a citizen of The Netherlands and presently residing in 4125 Riehen, Switzerland, hereby declare:

That I was awarded the degree of Drs in inorganic chemistry by the University of Leiden, The Netherlands, in 1982;

That I have been employed by Ciba Specialty Chemicals (formerly CIBA-GEIGY AG), Switzerland, as a chemist since 1997, and presently hold the position of Researcher Display Materials;

That I have been working in the field of electronic displays (cathode ray tubes and LCD's) for over 25 years and since joining Ciba in 1997 have been engaged researching materials for color filters for LCD's with special interest in pigments, latent pigments, binder systems and reactive acrylate monomers and their application in colour filter resists. I have published a number of articles and I am the inventor and co-inventor of a number of patents, including US Patents in fields closely related to the display materials application.

That I am an inventor on U.S. Patent Application Serial No. 10/523,742.

That the experiments described in the following have been made under my supervision and the evaluation of the results has been done by myself.

BACKGROUND

The present invention provides green color filters comprising specific green pigments. The standard for green color filters is Pigment Green 36 which is a Cu phthalocyanine having 4-9 Br and 8-2 Cl atoms. Unfortunately, this pigment has a broad transmission making it difficult to reach good color saturation while maintaining high transmission. A greenish yellow pigment must be added to adjust the transmission window which further reduces the desired transmission.

US. Pat. Appl. No. 2002/00451, cited by the examiner, attempts to achieve both color saturation and high transmission in a green color filter resist by using combinations of phthalocyanine dyes in combination with yellow pigments. Although pigments and dyes share structural features, there are significant differences. On the one hand, while dyes are soluble, pigments have to be dispersed. This can be difficult for some pigments in demanding applications such as color filters. On the other hand, the insolubility of a pigment can be advantageous, for example, in the present case it makes the instant pigments inert to the radical polymerisation which occurs during the preparation of the color filter pattern.

The fact that the phthalocyanines of the present invention actually behave as pigments and not as dyes is, in itself, surprising. Although OR-substituted Cu-phthalocyanines (CuPc) similar to those used in the invention are known to be soluble in a variety of solvents, it was surprisingly found that the instantly substituted phthalocyanines do not dissolve in color filter resist formulations.

It was further found that the absorption/transmission behavior of the instant pigments was ideal for use in green color filters as the pigments not only exhibit broad absorptions, blocking unwanted wavelengths of light, they also have a narrow window of transmission with sharp cutoffs on either side of the transmission max leading to transmission of clean, intense color.

These, and other advantages are shown in the experiments below.

EXPERIMENTAL

The experiments herein compare Solvent Blue 67, the blue CuPc dye used in the examples of Machiguchi et al., US 2002/00451, to the green pigment (tetra- α -hydroxy copper phthalocyanine according to Example 1 of the instant application, herein designated as PG2808).

Example 1: Stability during radical polymerization.

A) Solvent Blue 67, no photo-curing

0.4 g of P.Y.150 are dispersed in a Skandex for 3 hours with 0.4 g of a dispersant (EFKA 4340), 3.2 g of a binder (benzyl-methacrylate-methacrylic acid-copolymer; 25% solution in PGMEA) and 7.6 g of PGMEA. At the end of the dispersion 0.6 g of Solvent Blue 67 are added. The resulting low viscous dispersion is spin coated on a glass substrate at 1000 rpm for 30 seconds and dried at 100 °C, postbaked at 200 °C for 5 minutes on a hot plate.

B) Solvent Blue 67, photo-cured

The procedure of A is repeated, but a photoinitiator (Irgacure OXE 02) is added, and the resulting coating is additionally exposed to UV after drying at 100 °C with a medium pressure Mercury lamp for about 1 min (UV dose about 100-150 mL/cm²).

C) PG2808, no photo-curing

0.6 g of PG2808 and 0.4 g P.Y.150 are dispersed in a Skandex for 3 hours with 0.4 g of a dispersant (EFKA 4340), 3.2 g of a binder (benzyl-methacrylate-methacrylic acid-copolymer; 25% solution in PGMEA) and 7.6 g of PGMEA. The resulting low viscous dispersion is spin coated on a glass substrate at 1000 rpm for 30 seconds and dried at 100 °C, postbaked at 200 °C for 5 minutes on a hot plate.

D) PG2808, with photo-curing

The procedure of C is repeated, but a photoinitiator (Irgacure OXE 02) is added, and the resulting coating is additionally exposed to UV after drying at 100 °C with a medium pressure Mercury lamp for about 1 min (UV dose about 100-150 mL/cm²).

The transmission of mixtures of each colorant with Pigment Yellow 150, an azomethine metal complex added to assist in blocking the blue light below ~ 450nm, is measured before and after curing.

Figure 1 (mixture of PG2808 and P.Y. 150) shows that the transmission of the colorant mixture does not substantially change before and after radical polymerization, whereas in figure 2 (mixture of Solvent Blue 67 and P.Y. 150) the increase seen in the transmission between 600 to 700 nm relates to a reduction in the concentration of the blue dye. Figure 2 also displays an undesirable, large transmission between 700 and 800 nm.

Fig. 1: PG2808 / P.Y. 150

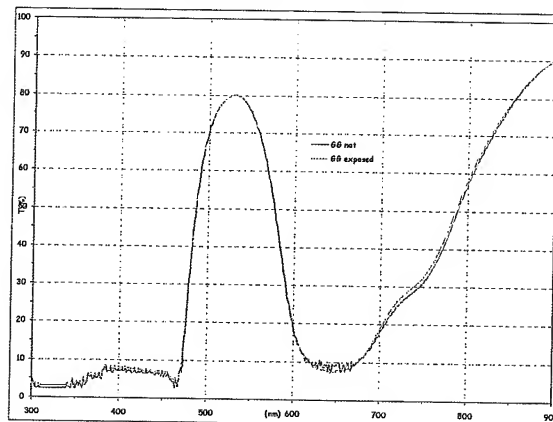
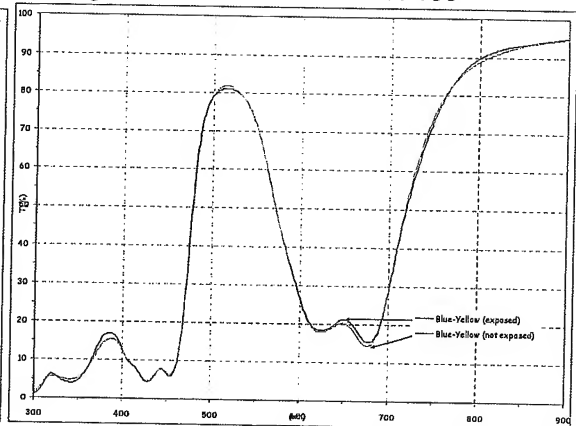


Fig. 2: Solvent Blue 67 / P.Y. 150

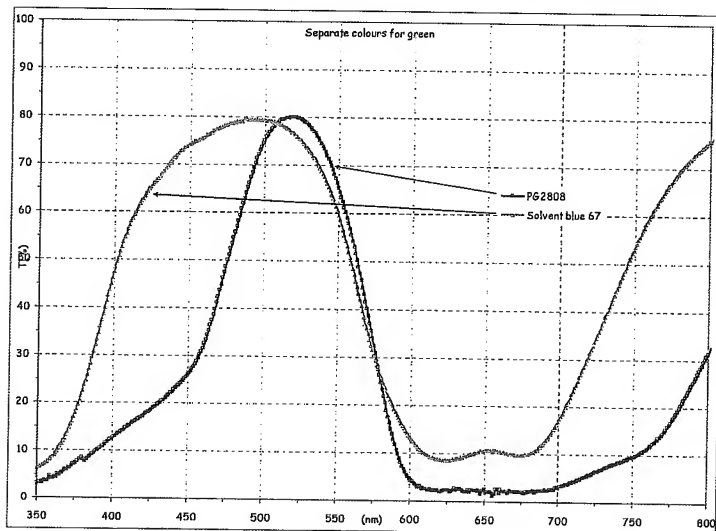


Example 2: Transmission and color.

A further surprising advantage of the instant pigment over the dye of US 2002/00451 is clearly illustrated by comparing the transmission spectra of the instant pigment (without P.Y. 150) vs the dye (without P.Y. 150). Figure 3 shows the spectra of Solvent Blue 67 and the instant green pigment, PG2808, wherein the spectra of the blue and green colorant are normalized to the same maximum transmission. (Comparison to Solvent Blue 67 continues not only due to the Examiners citation of Machiguchi et. al., but also because I am aware of no green dyes currently useful for the instant color resists.)

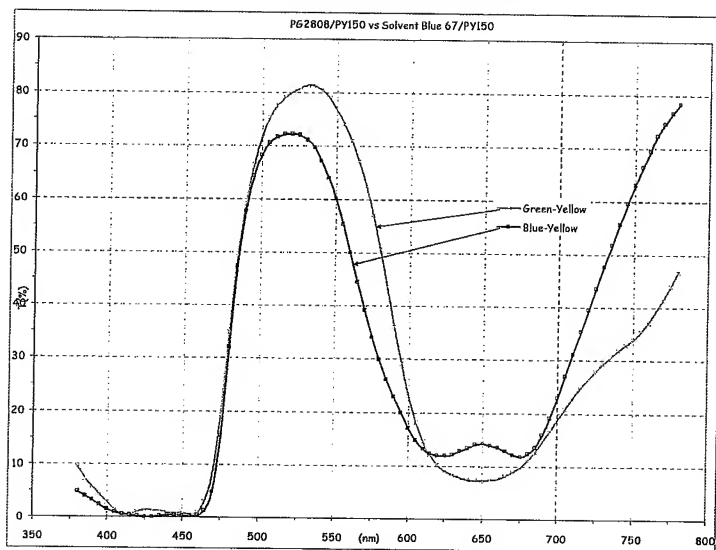
The areas under the peaks below represent the light which passes through the sample, the other light being blocked. One clearly sees that the pigment of the invention allows only a narrow selection of light to pass through, whereas the dye of US 2002/00451 allows significantly more blue light (400-450nm) and red light (above 700 nm) to pass through as well as more light near 650nm.

Figure 3. The darker line represents the instant pigment:

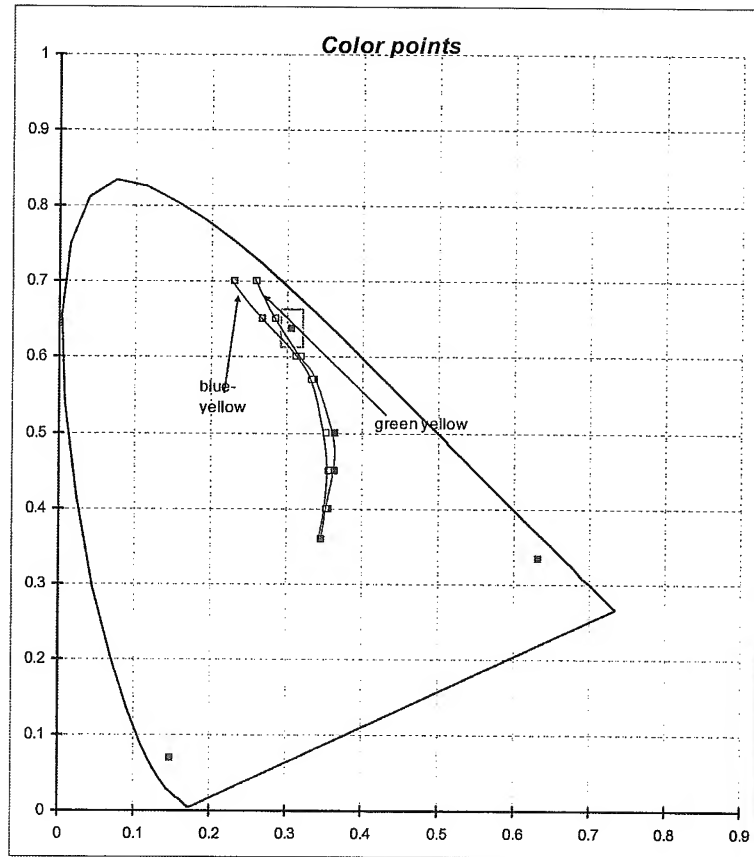


The instant pigment clearly results in broader absorptions, but it also, surprisingly displays a much sharper transmission band vs the dye.

Color and transmission of a 60/40 mixture of Solvent Blue 67 and P.Y.150 and a 60/40 mixture of the green pigment PG2808 and P.Y.150 are compared at the same color saturation ($y = 0.60$, see graph below). Clearly, the green/yellow mixture of the invention (the lighter line) has a higher transmission at ~ 535 nm and a lower transmission at ~ 650 .



The green pigment and blue dye are each mixed with PY 150 to generate color points as comparable as possible. The color points and saturation curves of the blue/yellow (dye) mixture and the green/yellow (pigment) mixture for several film thicknesses are compared below (x=hue, y= color saturation, Y%=transmission). The target color point is inside the rectangle, x =~0.30.



	x	y	Y(%)
blue-yellow	0.3565	0.4	92.9
	0.3642	0.45	83.9
	0.3633	0.5	73.9
	0.3361	0.57	55.9
	0.3126	0.6	46.3
	0.2665	0.65	28.9
	0.2298	0.7	6.3
green-yellow	0.3527	0.4	93.1
	0.3562	0.45	85.1
	0.3531	0.5	77.1
	0.3334	0.57	64.4
	0.318	0.6	57.8
	0.2853	0.65	43.7
	0.2587	0.7	21.6

As can be seen in the table and graph above, very similar colors i.e., hue (x), are prepared from the two systems. However, as can be seen in the table, the transmissions (Y%) at the same colour saturation (y) are much lower for the blue dye-yellow pigment mixture than for the green pigment-yellow pigment mixture, due in larger part to the greater amount of PY 150 needed for the dye mixture. Further, not only is the transmission at the target color point about 25% higher for the green pigment-yellow pigment mix, the Blue Dye-Yellow mixture remains slightly too blue, but correcting the hue by adding more yellow will result in still lower transmissions.

DISCUSSION

A color filter requires that only light of a specific color be allowed to pass through. Color filters for high end applications also require stringent and demanding manufacturing protocols. The desired colors are well defined, and, as discussed in the specification, e.g., the bottom of page 5, transmission within a narrow window is required. When the colorants used in a color filter have broad transmission curves, attaining color saturation becomes difficult and requires the use of larger quantities of pigment or dye, which will also block some of the desired light, reducing the transparency in the selected window and diminishing the desired transmission.

One means for preparing a green color resist is to mix a blue dye, e.g., phthalocyanine dye, with a yellow pigment. Blue dyes are typically encountered as there are no useful green dyes. The blue dyes used in the art have broad transmissions in the blue and cyan-green areas. In order to get enough colour saturation the concentration of colorants needs to be raised, in particular the yellow pigment, resulting in significantly lower transmissions.

The instant green pigments offer surprising advantages over the use of blue dyes. One advantage is the fact that these particular $\text{CuPc}(\text{OH})_4$ pigments are not soluble in the resist formulations as are other OR-substituted CuPc's. As a result, the instant pigments do not react or degrade during the radical polymerizations encountered in the process of preparing high quality color filters, whereas the soluble dyes are partially destroyed.

Another advantage of the pigments is that they have broader absorptions and more narrow transmissions than similar dyes. This makes color saturation possible at lower concentrations of colorant resulting in greater transparency and transmission at the desired wavelengths.

It must be remembered that pigments attain much of their coloristic properties from their physical structure, not just from their chemical composition. For example, different crystal forms of pigments have different colors, different particle sizes have different color depths and intensities as well as shades of the color and different usable lifetimes. The physical integrity of the pigment particle (crystalline structure) must therefore remain intact. (As already stated, the mere fact that the instant CuPc's remain insoluble pigments in this use is surprising.) These effects greatly impact the suitability of using a dye or a pigment in a particular process. Therefore, not only are pigments and dyes not always functional equivalents, the properties, including specific coloristic properties, of pigments with similar chemistry is not always predictable.

It has been found, quite surprisingly, that the instant pigments have ideal coloristic properties for green color filters and require less color corrections than similar dyes and result in higher transmissions. I know of no CuPc dyes with the same green hue as the instant pigment.

As color filter expert, the above advantages for the instant phthalocyanines are highly significant and could not be predicted.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed 21 of April, 2009



Gerardus de Keyzer,